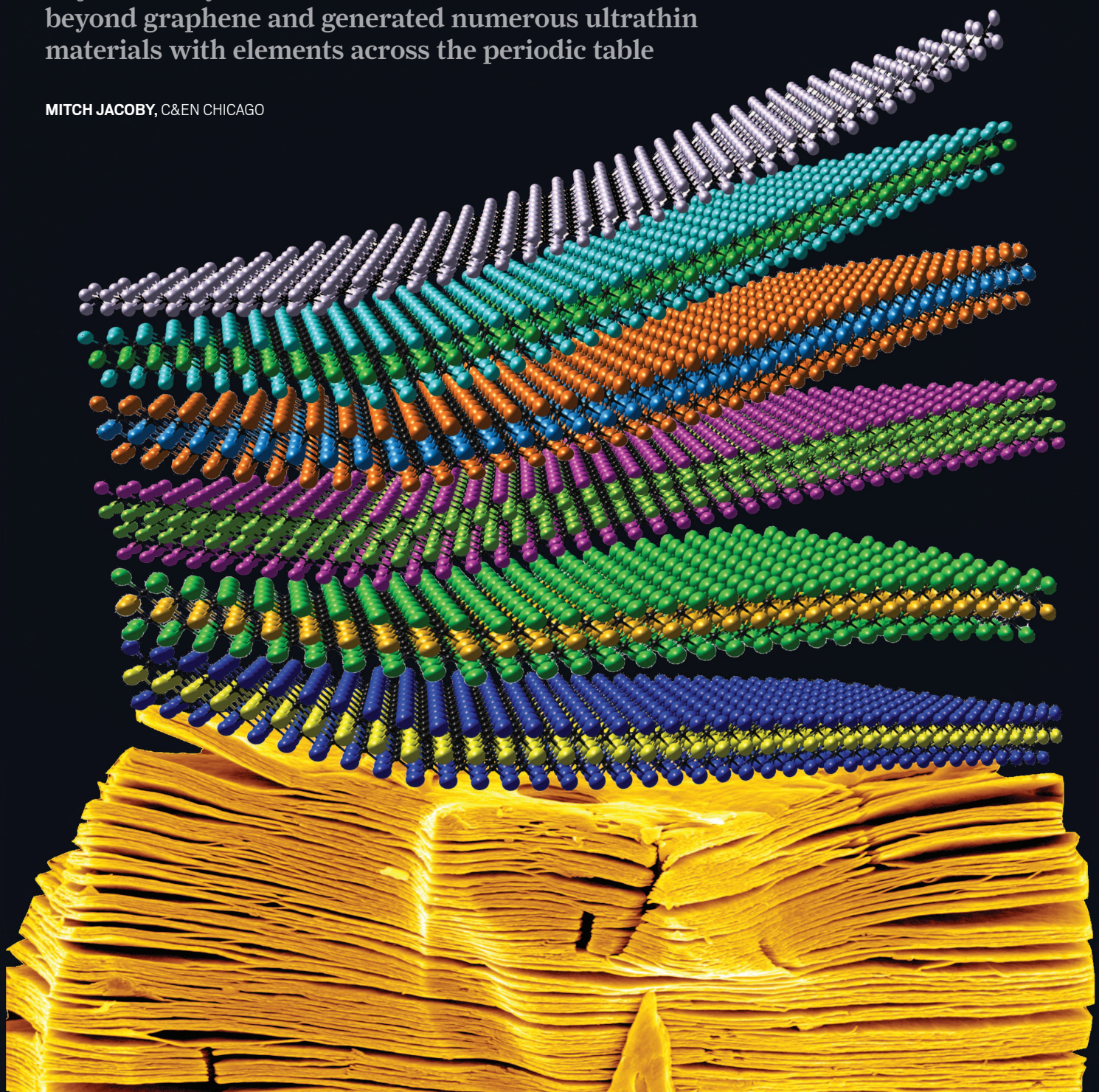
2-D materials stack up

In just a few years, researchers have moved well beyond graphene and generated numerous ultrathin materials with elements across the periodic table

MITCH JACOBY, C&EN CHICAGO



This stack of separable Ti_3C_2 sheets (yellow micrograph, bottom) is one example of a MXene. Researchers have made a large variety of MXenes, which exhibit M_2X, M_3X_2, and M_4X_3 stoichiometries, in which M is an early transition metal and X is carbon or nitrogen (models, top).

Despite being just a single layer of carbon atoms, graphene sure can excite engineers and scientists. Unlike bulk graphite, the ultrathin material boasts flexibility, strength, and possibly enticing electronic properties for researchers to exploit in novel applications. Graphene mania crescendoed in 2010 when the material's discovery was the subject of that year's Nobel Prize in Physics. Since that time, researchers worldwide have been enthralled with vanishingly thin films and have succeeded in preparing a wide variety of so-called two-dimensional materials beyond graphene.

This story is about those other 2-D materials. They hail from across the periodic table and include an assortment of transition metals, carbon-group elements, chalcogenides, and others. Researchers are taking this trip through the periodic table in search of the ultrathin because, like graphene, some of the materials they're making sport impressive properties that surpass those of their thicker counterparts.

These 2-D materials encompass electrical conductors, insulators, and semiconductors. They include chemically inert materials as well as ones that are readily modified through chemistry. And because these materials are ultrathin, they tend to be flexible and transparent, ideal features for new types of energy storage devices, high-speed and wearable electronics, and other applications.

So what exactly does it mean for a material to be 2-D?

The definition depends on whom you ask. The dozen or so scientists C&EN contacted for this story stipulate that to qualify as 2-D, the material needs to be well ordered, relatively expansive in two dimensions, and ultrathin in the third dimension—on the atomic or molecular scale. Beyond that there is little agreement.

For example, what passes as "ultrathin" can vary depending on the material and application. The graphene work that netted the Nobel Prize for Andre K. Geim and Konstantin S. (Kostya) Novoselov involved isolating one-atom-thin sheets of carbon from graphite. But researchers still consider a sample to be graphene—and a sample still exhibits some unique graphene properties—even when it is two, three, and more layers thick. In those cases, they're just described as bilayer or few-layer graphene.

So where do researchers draw the ultrathin line? How many atoms in thickness can a metal carbide or film of silicon be before it transitions from a 2-D material to a "thick" layered material or a coating?

In general, scientists seem uninterested in assigning a strict limit to the thickness of these materials. But the thickness does matter when researchers are thinking about applications.

"Mathematics is good at rigorous definitions, but this isn't mathematics; it's chemistry and physics," says Boris I. Yakobson, a Rice University theoretician and materials scientist who studies 2-D materials. "It's good to have definitions, but often, they're not flexible enough to reflect reality."

The other gray area in defining 2-D is whether to require that these ultrathin films can be manipulated, picked up, and transferred.

Two-dimensional ma-

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>
> **—Yury Gogotsi,** Drexel University

In brief

In the excitement after the isolation of graphene, materials chemists and other scientists began scrutinizing the periodic table for opportunities to make other molecularly thin materials. Driven by the chance to explore uncharted scientific territory and to discover technologically useful materials, these researchers quickly produced many examples of so-called two-dimensional materials beyond graphene. The growing list now includes a large set of metal carbides (MXenes), a family of single-element graphene analogs (Xenes), a number of transition metal dichalcogenides, ultrathin organic crystals, and two-component nitrides.

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terials can be grown via vapor deposition of precursor molecules or isolated from a multilayer crystal or flake. But a material doesn't need to be freestanding or separable from the surface on which it was grown or derived to gain membership in the 2-D club.

Some of the materials in this story are freestanding; others are not. Not being freestanding, though, can hinder a material's use in applications. Eventually, researchers may come up with ways to separate 2-D materials that currently cannot be freed. That kind of advance will likely open the door to developing new applications, and ultimately, new applications will continue driving this field.

One reason so many research groups focus on 2-D materials is because of the unique collection of properties the materials exhibit. For example, 2-D versions of silicon (silicene), phosphorus (phosphorene), and some of carbon's other neighbors in the periodic table are semiconductors with band gaps and other electronic properties that, in principle, can be tuned more easily than they can in the bulk materials. That's because those properties depend greatly on layer thickness and doping.

Adding one layer to a single-layer material significantly alters its thickness. Not so for the bulk counterpart. And because all the atoms in a single-layer film are exposed, they are all accessible for chemical modification, which can further modify electronic properties. In a bulk material, most of the atoms are buried under the surface and are inaccessible for chemical modification.

The thinness of 2-D materials also allows electric fields to leak through them and interact with other materials below them. This feature could allow researchers to control the electronic properties of those underlying layers, according to Mark C. Hersam of Northwestern University, a specialist in semiconductor devices. Scientists can use that unique electrostatic penetration to make new types of diodes, memory circuits, and other devices that would be impossible to make with bulk semiconductors, he says.

"These unique properties may lead to new and useful applications, and that is part of their appeal, but I think that's secondary," says Yury Gogotsi, who leads a nanomaterials research group at Drexel University. "More importantly, we're learning to use 2-D materials as building blocks to custom make modern materials." Gogotsi and others envision developing methods for combining, either by stacking or by juxtaposing laterally, various types of 2-D materials with distinct sets of properties to build materials with truly novel features on demand.

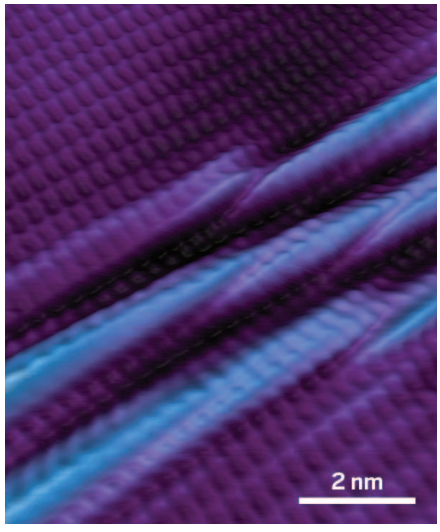
Regardless of whether researchers uncover truly unique properties in 2-D materials, the work is providing scientists with an exciting opportunity to trek through unexplored territory, Yakobson says.

"Mathematics is good at rigorous definitions, but this isn't mathematics; it's chemistry and physics."

—**Boris I. Yakobson,** Rice University

Gogotsi agrees: "Whether you're a five-year-old child playing with a new toy at home or a 50-year-old child playing with a new toy in the lab, it's fun. When people see new toys, they get excited."

These new toys can be divided into five major groups: MXenes, Xenes, organic materials, transition metal dichalcogenides, and nitrides. Some groups have many members; others few. Some have already been used in demonstration devices, while others are still laboratory curiosities. But they have all taken researchers into the ultrathin world. The rest of the story provides brief glimpses of four of these groups. To explore all the groups and take a 2-D trip across the periodic table, go to cenm.ag/2dmaterials.



Grown via vapor deposition of boron, atomically thin borophene adopts a buckled structure, as seen in this atomic-resolution scanning tunneling micrograph.

MXenes: A 2-D surprise

About six years ago, Gogotsi and Michel W. Barsoum, a materials scientist at Drexel University, were searching for ways to make high-performance lithium-ion battery anodes. The team had experience with a promising family of electrically conducting carbides and nitrides known as the MAX phases. *M* refers to early transition metals, *A* symbolizes main-group elements such as aluminum and silicon, and *X* represents carbon or nitrogen.

The team wanted to boost the efficiency with which Li ions reversibly insert themselves in the anodes during charging and discharging. So they tried to make room for the ions by using concentrated hydrofluoric acid to selectively remove aluminum atoms from Ti_3AlC_2 and other MAX phases. The process improved the materials' performance in batteries. It also completely removed the Al layers and exfoliated the crystals into ultrathin, 2-D, graphenelike sheets of Ti_3C_2.

The team showed that this exfoliation process can also produce Ti_2C, Ta_4C_3, $(Ti_{0.5}Nb_{0.5})_2C$, $(V_{0.5}Cr_{0.5})_3C_2$, Ti_3CN, and other materials. They named the family of materials MXenes, which is pronounced "maxenes" to deliberately rhyme with graphene. The researchers have now prepared nearly 30 MXenes, and many more have been predicted (*Nat. Rev. Mater.* 2017, DOI: 10.1038/natrevmats.2016.98).

Many research groups are studying these 2-D materials, but the Drexel scientists remain at the forefront. They have devised a method for making MXene-polymer composites that are electrically conductive, strong, flexible, and durable—ideal properties for electrodes in energy storage and wearable technology (*Proc. Natl. Acad. Sci. USA* 2014, DOI: 10.1073/pnas.1414215111). The Drexel team has also demonstrated that MXenes can serve as lightweight, inexpensive shielding materials to protect cell phones and other devices from electromagnetic interference (*Science* 2016, DOI: 10.1126/science.aag2421). They've also recently started making 100-g batches of MXenes with a custom-made reactor.

Xenes: Elements go solo

Carbon isn't the only element that can form ultrathin, monoatomic sheets. In the past few years, elements that are clustered in the periodic table near carbon (B, Si, P, Ge, and Sn) have jumped onto the 2-D stage. Scientists refer to this family collectively as Xenes, where *X* represents the name of the element and "ene" comes from graphene. These materials, which include borophene, silicene, phosphorene, germanene, and

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The 2-D world

Scientists have developed five groups of 2-D materials from elements across the periodic table. The key elements in each are color coded by family (below).

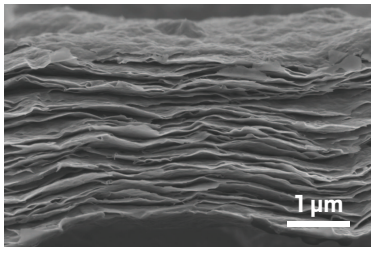
To take a more in-depth look at 2-D materials beyond graphene, go to **cenm.ag/2dmaterials.**

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

MXenes

Ti_3C_2, Ta_4C_3, and others

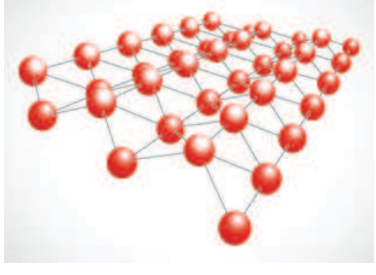
Properties & potential applications: MXenes—transition metal carbides and nitrides including Ti, Zr, V, Ta, and others—feature high strength, flexibility, conductivity, and chemical tunability. Possible applications include energy storage and electromagnetic shielding.



Xenes

B, Si, P, Ge, and Sn

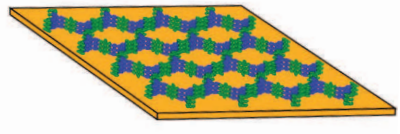
Properties & potential applications: These materials' atoms arrange as buckled sheets in a honeycomb pattern. Xene band-gap and charge-transport properties make them candidates for fast, flexible electronics and energy storage devices.



Organic materials

C

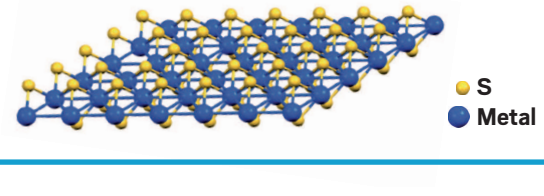
Properties & potential applications: Covalent organic frameworks and other organic compounds composed of stacked molecular sheets are promising candidates for nanoporous filters and membranes, biosensors, and optoelectronic devices.



Transition metal dichalcogenides

MoS_2, WS_2, and others

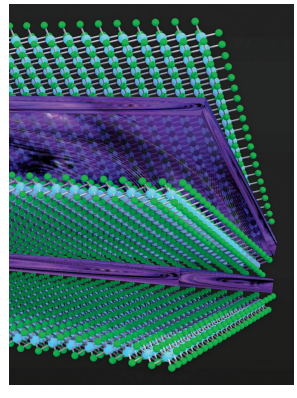
Properties & potential applications: Because of their pronounced band gaps, these sheetlike semiconductors have been used to fabricate transistors and other circuit elements for lightweight, flexible electronics.



Nitrides

GaN, BN, and Ca_2N

Properties & potential applications: This group of materials includes electrical insulators and conductors that could be used in high-speed, transparent, flexible electronics.



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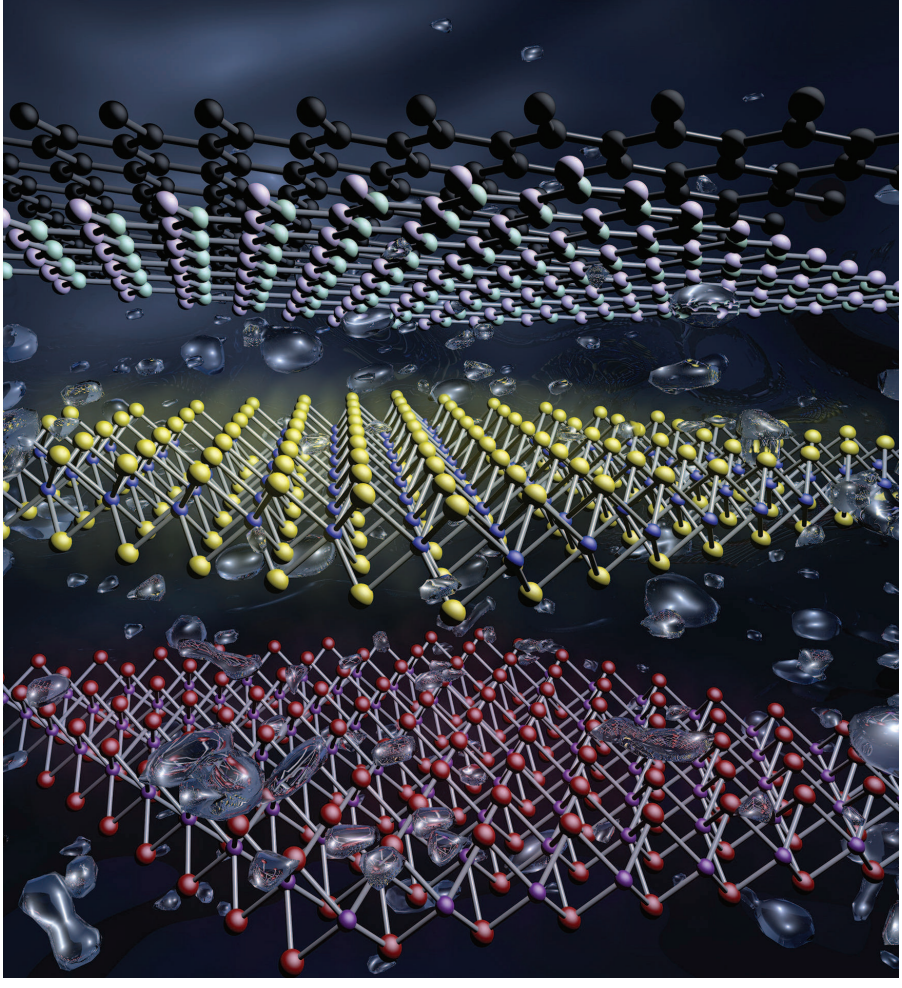

This artist's rendition of 2-D materials in water depicts a research trend to develop inexpensive, solution-based processing methods for these materials. Shown here are (from top) graphene (black); hexagonal boron nitride (B is green, N is pink); molybdenum disulfide (Mo is blue, S is yellow), and tungsten diselenide (W is purple, Se is red).

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stanene, all share a buckled or corrugated shape—unlike graphene's flat sheets—and sport atoms arranged in a honeycomb lattice. Silicene, phosphorene, and borophene are the most studied of the family.

Silicon is used in bulk throughout the electronics industry. But researchers in the U.S. and Italy showed that the element can also be useful in its 2-D form. The team grew a 2-D silicene layer on silver and capped it with a protective layer of alumina. The researchers used the single layer of silicon atoms as the channel in a field-effect transistor, which shuttles charge from the source to the drain electrodes (*Nat. Nanotechnol.* 2015, DOI: 10.1038/nnano.2014.325).

Phosphorene could also be useful for making fast electronics because of its high charge mobility. But the material degrades upon exposure to air, thwarting efforts to use it. Northwestern's Hersam came up with one way around the problem. His group protects the material by treating flakes of black phosphorus, the starting material from which researchers isolate ultrathin phosphorene sheets, with a solution of a benzenediazonium derivative that passivates and protects the material (*Nat. Chem.* 2016, DOI: 10.1038/nchem.2505).

Unlike other materials in this group, borophene has metallic character, making it potentially useful for connecting elements in circuits and acting as a transparent conductor. This Xene made its debut when two research teams used vapor deposition methods to grow one-atom-thick boron films on metals (*Angew. Chem. Int. Ed.* 2015, DOI: 10.1002/anie.201509285; *Science* 2015, DOI: 10.1126/science.aad1080). But to use borophene in applications will require separating the material intact from its support, something that has yet to be demonstrated.

Organic materials: Carbon moves beyond graphene

It's not just single elements, or combinations of a few elements, that can enter the 2-D world. Multielement organic molecules also form ultrathin materials.

The richness of organic chemistry offers a unique opportunity to customize the properties of these organic 2-D materials to make chemical and biological sensors, chemically selective membranes, and electronic devices. But forming these 2-D crystals is challenging because of covalent bonding between layers.

One solution has been to exfoliate covalent organic frameworks (COFs), which are crystalline porous polymers. Sonicating COFs thins them, but how thin they get depends on the strength of the bonding within a single layer versus the strength of the bonding between adjacent layers. If the interlayer bonding is stronger, the COFs resist thinning. Common boronate-linked COFs tend to do this. But as Northwestern's William R. Dichtel showed, sonicating hydrazone-linked COFs in dioxane and other common solvents yields bulk quantities of few-layer 2-D crystals (*J. Am. Chem. Soc.* 2013, DOI: 10.1021/ja4082431n).

A. Dieter Schlüter of the Swiss Federal Institute of Technology (ETH), Zurich, demonstrated a different approach and applied it to a related material—metal organic frameworks (MOFs), which are porous crystalline materials composed of metal ions joined by organic linkers. His team prepared a series of ultrathin crystals made of tri- and hexa-functionalized terpyridine-based groups joined by Zn^{2+} ions. The researchers then selectively exchanged the zinc ions with Fe^{2+}, Pb^{2+}, and Co^{2+}, thereby making a new set of 2-D MOFs (*J. Am. Chem. Soc.* 2014, DOI: 10.1021/ja501849y).

Transition metal dichalcogenides: Scaling up

Numerous research groups have demonstrated that ultrathin layers of transition metal dichalcogenides such as MoS_2 and WS_2 can serve as key circuit components in fast electronics. But methods to make the thin films tend to be laborious and yield just tiny quantities of material.

To sidestep the slow production, Cornell University's Jiwoong Park used $Mo(CO)_6$ or $W(CO)_6$ as precursors in a chemical vapor deposition process to form films of MoS_2 and WS_2, respectively, that were only three atoms thick but covered an area of about 65 cm^2 (*Nature* 2015, DOI: 10.1038/nature14417). The films were high enough in quality to be used in field-effect transistors.

And last year, Northwestern's Hersam and coworkers reported a low-cost method for separating single- and bilayer ReS_2 through liquid-phase exfoliation based on ultrasonication followed by ultracentrifugation (*Nano Lett.* 2016, DOI: 10.1021/acs.nanolett.6b03584). ■